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54 Recording sheet having a colorant-absorbing layer.

57 A recording sheet comprising a substrate and a colorant absorbing layer made of a porous inorganic oxide, formed on the substrate, wherein said colorant absorbing layer contains an organic acid with the first acid dissociation exponent of at most 5, which has an aromatic nucleus or at least two carboxyl groups.

simply as the organic acid.

As a method for applying the above organic acid to the colorant absorbing layer, a method is preferably employed wherein a solution having the above organic acid dissolved in a suitable solvent is applied to the preliminarily formed colorant absorbing layer by a dipping method or by a spraying method. Otherwise, it is possible to employ a method wherein the above organic acid is mixed to the raw material for forming the colorant absorbing layer. In the method of applying the solution to the colorant absorbing layer, the solvent may suitably be selected depending upon the solubility of the organic acid. When the above organic acid is used in the form of a salt, there is a merit that water can be used as the solvent.

The content of the above organic acid is preferably from 0.05 to 7.5 wt%, based on the weight of the colorant absorbing layer. If the content of the above organic acid is less than 0.05 wt%, no adequate effects of the present invention tend to be obtained, whereby a color change of the recording sheet is likely to result, such being undesirable. If the content of the above organic acid exceeds 7.5 wt%, there will be no further increase in the effects for suppressing a color change. Not only that the absorptivity of the porous layer is likely to be impaired. More preferably, the content of the organic acid is from 0.5 to 5.5 wt%.

In the present invention, the colorant absorbing layer is a porous layer capable of absorbing and fixing colorants at the time of recording. The colorants include dyes and pigments. It is particularly preferred to employ a dye for recording, since it is thereby possible to obtain particularly high image quality. If the thickness of the colorant absorbing layer is too thin, the colorant can not adequately be supported, and only a printed record with a low color density will be obtained, such being undesirable. On the other hand, if it is too thick, there will be a drawback such that the strength of the colorant absorbing layer will decrease, or the transparency will decrease to impair the transparency or the quality of the printed matter, such being undesirable. A preferred thickness of the colorant absorbing layer is from 1 to 50  $\mu\text{m}$ .

The colorant absorbing layer is required to be a porous inorganic oxide. Specifically, it preferably has a structure having inorganic oxide particles bonded preferably by a binder. The material of such inorganic oxide particles is preferably silica or alumina, or a hydrate thereof. Particularly preferred is a pseudoboehmite porous layer, since it has good absorptivity and at the same time is capable of selectively adsorbing dyes, whereby it is possible to obtain clear records with high color densities by means of various types of recording systems. Here, the pseudoboehmite is an alumina hydrate of the compositional formula  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  (wherein  $x = 1$  to 1.5), and an agglomerate having a porous structure.

When the inorganic oxide is pseudoboehmite, the above organic acid is preferably incorporated in an amount within a range of from 0.2 to 30 mmol, more preferably from 1 to 20 mmol, per mol of Al atoms.

The pseudoboehmite porous layer preferably has a porous structure comprising pores with radii of from 1 to 10 nm and having a pore volume of from 0.3 to 1.0 cc/g, since such a layer has adequate absorptivity and transparency. Here, if the substrate is transparent, the recording sheet will also be transparent. If the substrate is opaque, it is possible to impart the necessary physical properties without impairing the quality of the substrate. In addition to such physical properties, it is further preferred that the average pore radius of the pseudoboehmite porous layer is from 3 to 7 nm. Here, the pore size distribution is measured by a nitrogen absorption/desorption method.

To prepare a pseudoboehmite porous layer having such a porous structure, it is preferred to coat on a substrate with a boehmite sol. As the boehmite sol, it is preferred to use a boehmite sol produced by hydrolysis of an aluminum alkoxide. As the coating method, it is preferred to employ a method which comprises preparing a slurry preferably by adding a binder to the boehmite sol, coating the slurry on the substrate by means of a roll coater, an air knife coater, a blade coater, a rod coater, a bar coater or a comma coater, followed by drying.

As the binder, an organic substance such as starch or its modified product, polyvinyl alcohol or its modified product, SBR latex, NBR latex, hydroxy cellulose, or polyvinylpyrrolidone, may be employed. The binder is used preferably in an amount of from 5 to 50 wt%, based on the inorganic oxide, since if the amount is small, the strength of the colorant absorbing layer tends to be inadequate, and on the other hand, if the amount is too large, the amount of ink to be absorbed or the amount of the colorant to be supported tends to be low.

In the present invention, various types of materials may be used for the substrate. For example, a plastic material, e.g. a polyester such as polyethylene terephthalate, polycarbonate, or a fluorine resin such as ETFE, or paper may suitably be employed. To such a substrate, corona discharge treatment or undercoating may be applied for the purpose of improving the adhesive strength of the colorant absorbing layer.

The function of the above organic acid in the present invention is not clearly understood. However, it is believed that the organic acid is adsorbed in the colorant absorbing layer and somehow suppresses the color development or adsorption of a component such as a plasticizer to a plastic which causes a color

Polyvinyl chloride films of the same size were overlaid on the coated sides of the respective recording sheets. The specimens were left in a room for 14 days, whereupon the presence or absence of yellowing at the edges of the sheets was visually checked. With respect to all recording sheets treated with the compounds in Table 2, no yellowing was observed even when at least three sheets were piled one on another.

Table 2

Organic acid in the treating solution	Solvent
Phthalic anhydride	Ethanol
Isophthalic acid	Ethanol
Terephthalic acid	Ethanol
Benzoic acid	Ethanol
Salicylic acid	Ethanol
Phenylacetic acid	Ethanol
Ammonium hydrogen phthalate	Water
Ammonium phthalate	Water
Pottasium hydrogen phthalate	Water
Benzenesulfonic acid	Water

## EXAMPLE 3

With respect to a sheet of coated paper obtained by coating porous silica on a paper substrate, an ethanol solution of phthalic acid with a concentration of 0.3M was impregnated from the coated side in the same manner as in Example 1, so that the solution was uniformly coated. The coated paper was vertically hung and dried in air, and then heated in a drum dryer at 140 °C for 4 minutes.

Polyvinyl chloride films of the same size were overlaid on the coated sides of the recording sheet thus obtained and a comparative recording sheet having no treatment applied. The specimens were left at room temperature for 14 days. Yellowing was observed on the edge of the non-treated sheet. Whereas, no such yellowing was observed with the treated sheets.

## EXAMPLE 4

The colorant absorbing layer side of the recording sheet obtained in Example 1 was dipped in an ethanol solution or an aqueous solution of a chain-type polybasic carboxylic acid or its salt as identified in Table 3 at a concentration of 0.2 mol/l, so that the solution was uniformly coated. The coated sheet was vertically hung and dried in air, and then heated in a drum dryer at 140 °C for 4 minutes.

Polyvinyl chloride films of the same size were overlaid on the coated sides of the respective recording sheets thus obtained. The specimens were left in a room for 14 days. With the respective recording sheets, no yellowing was observed.

Table 3

Organic acid in the treating solution	Solvent
Succinic acid	Ethanol
Succinic anhydride	Ethanol
Adipic acid	Ethanol
Monoammonium adipate	Ethanol
Maleic acid	Ethanol
Monoammonium maleate	Water
Malonic acid	Water
Oxalic acid	Water



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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 10 3603

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-4 775 594 (R.C.DESJARLAIS) * column 5, line 24 - line 46; claims 1,10; examples 2-3 * ---	1-10	B41N3/03 B41M1/30
X	DATABASE WPI Section Ch, Week 9244, Derwent Publications Ltd., London, GB; Class B41, AN 92-361876 ASAHI GLASS K.K. & JP-A-04 263 983 (ASAHI GLASS K.K.) 18 February 1991 * abstract * ---	1-10	
X	US-A-4 562 448 (H.WATANABE ET AL.) * column 2, line 20 - line 33 * * column 4, line 51 - line 53 * * column 5, line 36 - line 38 * ---	1,9	
X	EP-A-0 410 051 (TOMOEGAWA PAPER COMPANY LIMITED) * page 2, line 45 - page 3, line 9 * * page 4, line 10 - line 19; claim 1; examples 22-23 * -----	1,9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			B41M B41N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 June 1994	Examiner Bacon, A
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	